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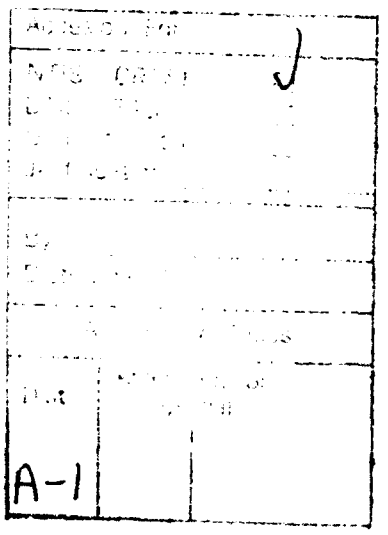

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FEMTOSECOND DYNAMICS, PHOTOEXCITATION AND ESR SPECTRA OF MX CHAIN SOLIDS

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Nonlinear adiabatic dynamics and ESR spectra associated with nonlinear excitations in MX chain (M=Pt, X=Cl,Br,I) materials are numerically studied within a discrete, 3/4-filled, two-band, tight-binding extended Peierls-Hubbard model. Both Hartree-Fock (HF) adiabatic molecular relaxation and molecular dynamics techniques are employed to investigate the time evolution of solitons, polarons, bipolarons in charge-density-wave (CDW) ground state materials. The time evolution of excitons, defect pairs and/or breathers is studied subsequent to photoexcitation. The ESR spectra associated with the resulting spin carrying nonlinear excitations such as neutral solitons, triplet excitons as well as electron and hole polarons are then calculated within the above model. The superhyperfine structure in the ESR spectra is attributed to a small spin density present on the halogen sublattice.

I. INTRODUCTION

Theoretical modeling, synthesis and experimental characterization of halogen bridged mixed valence linear chain MX materials have been described recently in great detail [1,2]. In particular, optical absorption, infrared and resonance Raman spectra were computed and compared with experimental data. Furthermore, we found that the mixed-halide MX materials exhibit photoinduced and intrinsic electron hole charge separation [3] which is potentially very useful for device applications. Here

we focus on the theoretical predictions for the (i) dynamics of photoexcitation and (ii) electron spin resonance (ESR) spectra in pure MX materials. It is worth noting that certain defect states, e.g. excitons, are inaccessible via impurity doping, but may be obtained during photoexcitation. This is illustrated below in the case of a weak CDW (delocalized) material PtI. The ESR spectra, however, is shown for a triplet exciton in the case of a strong CDW (localized) material PtCl. We present the results of theoretical calculations based on a discrete, 3/4-filled, two-band, tight-binding, Peierls-Hubbard Hamiltonian for representative parameter sets [1].

II. DYNAMICS AND PHOTOEXCITATION

We have investigated the photodecay channel subsequent to photoexcitation in the ground state as well as in the presence of nonlinear excitations and impurities using adiabatic molecular dynamics [1,4]. Photoexcitation was simulated numerically by manually removing an electron from an occupied state and instantaneously placing it in an unoccupied state. The system was allowed to evolve adiabatically with no further changes in electronic occupations. Fig. 1 shows the evolution on a PtI chain with 96 sites (48 Pt atoms and 48 I atoms) after a single electron is photoexcited across the Peierls gap, with the addition of the gap energy ($E_g \simeq 1.2$ eV) to the system. Periodic boundary conditions were employed. As is clear from Fig. 1(a), initially an exciton is formed within a phonon period. However, this exciton is unstable and evolves into a slowly separating kink-antikink pair. The electronic occupancies of the excited state necessitate that both of these kinks are neutral. Since the creation energy of the kink-antikink pair is smaller than the gap energy, the remaining energy goes partly into the kinetic energy of the kinks, partly into the acoustic phonons

and partly in the form of a small amplitude localized "breather" (phonon bound state) between the kinks. Such a breather, a temporally and spatially coherent state of optical phonons [4], is clearly visible in Fig. 1(a). Alternatively, a breather is a charge-neutral, spatially localized, time-periodic, in general persistent, nonlinear lattice excitation which has important implications for subpicosecond time-resolved absorption experiments. It has distinct signatures in the intragap absorption. Since PtI is a delocalized system the initially formed exciton is extended over about 40 sites. Similarly, the breather is also quite extended.

Fig. 1(b) shows the time evolution of associated energy levels, in particular the characteristic gap states of a kink pair. Within ~200 femtoseconds two continuum states are pulled into one (almost) degenerate midgap state indicating that the initial bound electron hole pair (exciton) quickly evolves into a kink-antikink pair. At the same time a breather level oscillates about the conduction band edge into the gap and persists with a time period larger than the phonon period. We have also studied dynamics of photoexcitation in PtCl and PtBr. Unlike PtI, at later times lattice discreteness effects hinder complete separation of the kink-antikink pair in PtCl which is a very localized CDW system.

III. ESR SPECTRA

We calculated the electron spin resonance (ESR) spectra associated with spin carrying nonlinear excitations such as neutral solitons, triplet excitons as well as electron and hole polarons for pure MX materials within the same two-band model used for the dynamics calculations. Our results contrast a strongly distorted CDW material, PtCl with that of a very weak CDW material, PtI. The excitations are

quite localized in PtCl whereas they are very extended in PtI. We attribute the superhyperfine structure in the ESR spectra to a small spin density present on the halogen sublattice. These theoretical predictions are compared with the experimental ESR data [5] on photoinduced defects in pure MX materials. We have also computed ESR spectra for mixed-halide MX materials.

For a given nonlinear excitation (polaron, *etc.*) we first numerically computed the Hartree-Fock (HF) spin density on each site of an MX chain. Next, these spin densities were appropriately weighted for various lines according to a quantum mechanical description based on the relative abundance of isotopes, their spin and g-factors (built into the numerical code). The field orientation dependence, (i.e., the dipole-dipole interaction created by the coupling of magnetic field generated by electron motion with nuclear spin) is also explicitly included within the local density approximation (LDA). However, at present we have neglected dynamical effects on the line shape such as spin-flip and coherent soliton motion. Each ESR line is Lorentzian broadened to mimic experimental line width.

For illustrative purposes, we show in Fig. 2 the calculated ESR spectrum for a triplet exciton in PtCl. Five main peaks (hyperfine structure) are clearly visible. Superimposed on these peaks is a small amplitude modulation (superhyperfine structure). A careful analysis of the spin densities reveals that the hyperfine structure arises from two parallel spins on two neighboring metal (Pt) ions in an exciton (a triplet exciton can be thought of as a bound state of an electron and a hole polaron with parallel spins). Most of the spin density ($\sim$95%) is on these two Pt atoms. However, the remaining spin density ($\sim$5%) is distributed over three Cl ions around and between the two Pt ions. This small spin density on the halogen ions is sufficient

to produce the superhyperfine structure. We emphasize here that since the halogen sublattice is not explicitly included in a one-band model, the latter will not be able to reproduce the superhyperfine structure. The experimentally observed ESR spectra [5] (not shown here) from photoinduced defects in PtCl resembles rather well with the calculated spectra (Fig. 2). Nevertheless, whether it arises from a triplet exciton, a kink-antikink pair or an electron and hole polaron pair remains an open question for the time being, although the evidence points more towards a polaron pair.

I. CONCLUSIONS

We have presented illustrative examples of theoretically calculated photodecay channel and ESR spectrum. Investigations of the influence of Coulomb interactions (both on-site and inter-site Hubbard terms), site and bond impurities on the photodecay channel are in progress in addition to the dynamics and ESR studies for mixed-halide MX materials. We believe that these studies will elucidate the processes of photoinduced charge transfer and self-doping in mixed-halide chains.

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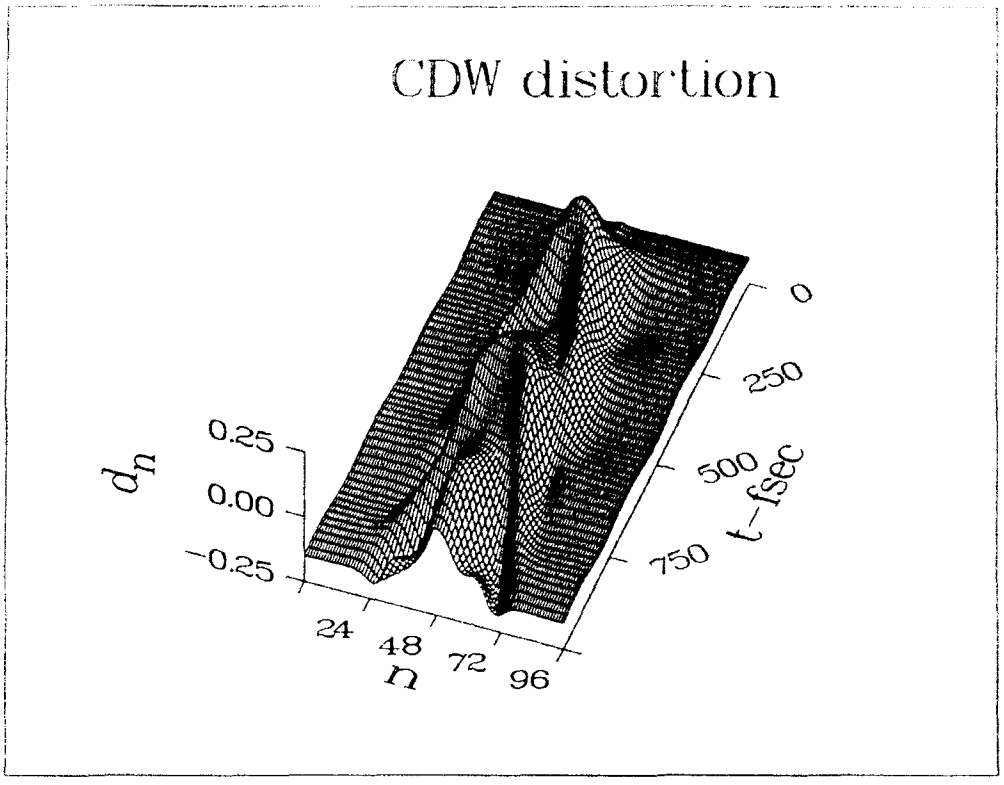
FIGURE CAPTIONS:

Fig. 1. Dynamics of photoexcitation in PtI: (a) CDW distortion as a function of time in units of 10^{-15} seconds. For clarity the negative of CDW distortion is plotted. (b) Energy levels as a function of time for photoexcitation of the ground state.

Fig. 2. The calculated ESR spectrum for a triplet exciton on a PtCl Chain. The horizontal axis gives peak positions in terms of scaled magnetic field while the vertical axis represents peak intensity in arbitrary units.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500
750
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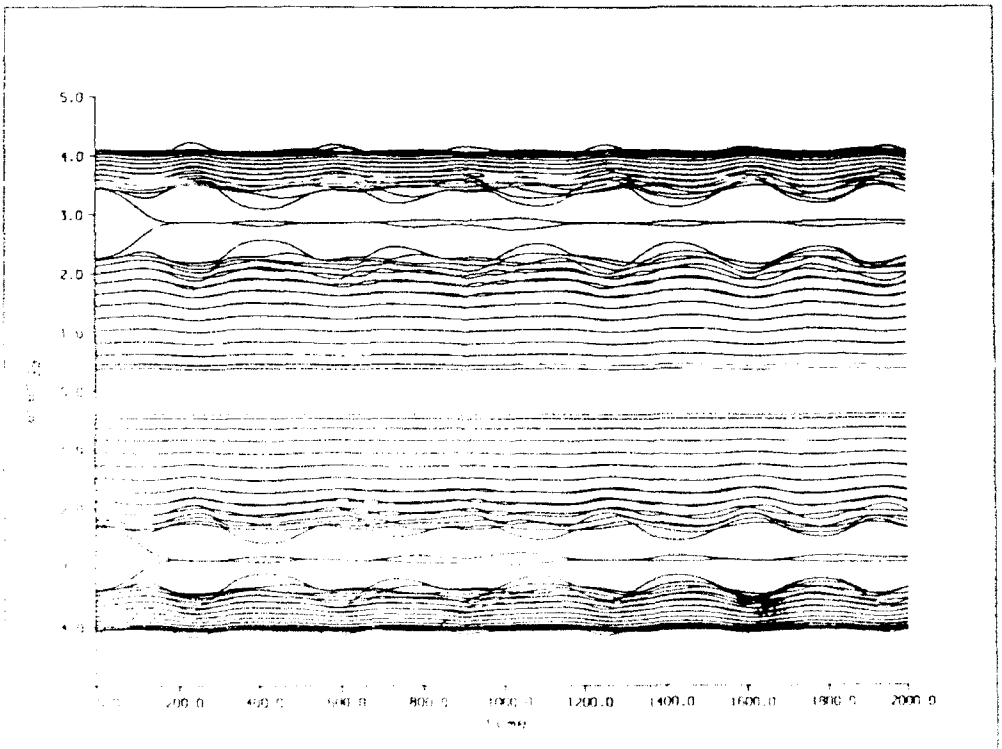
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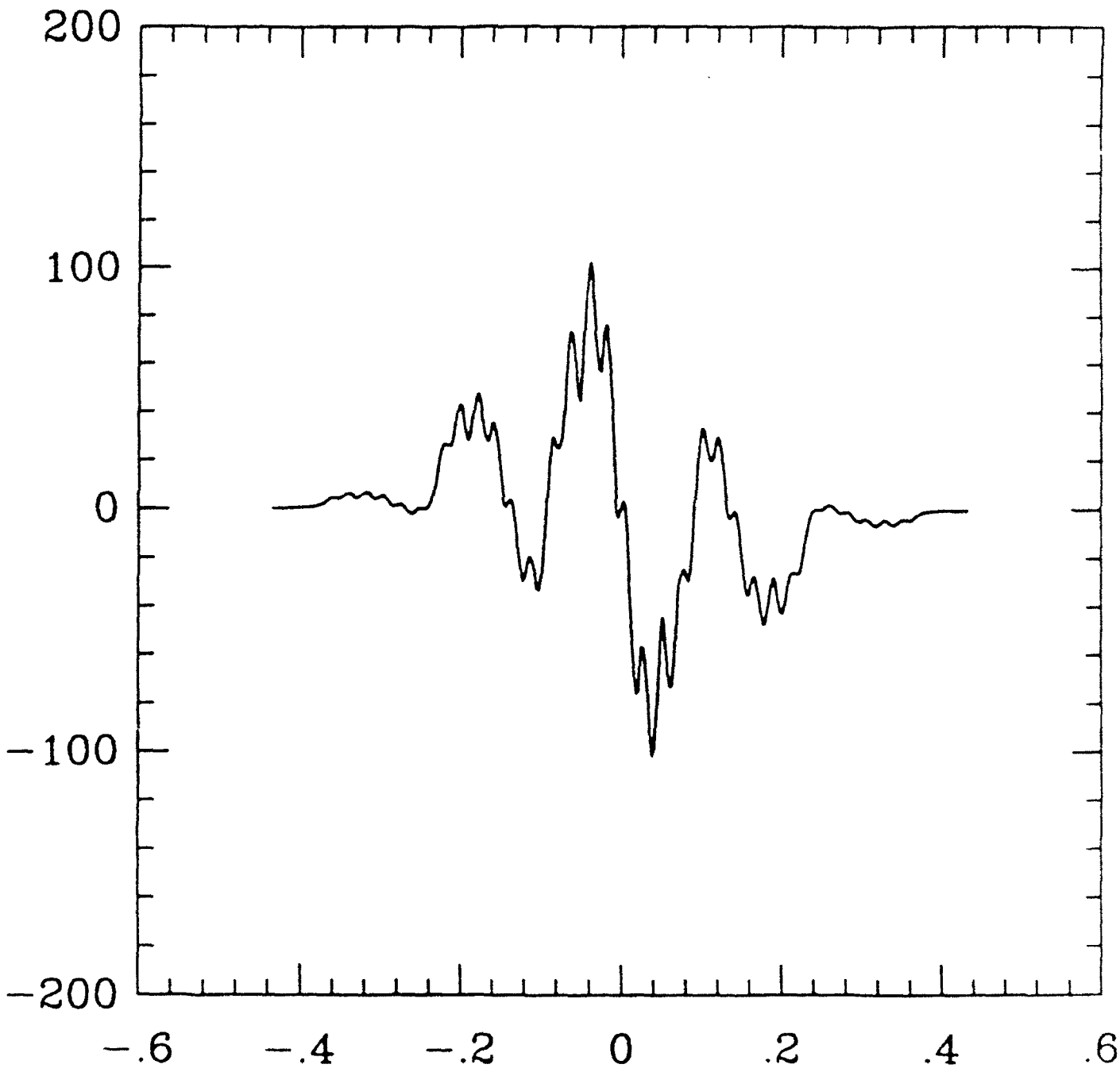
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